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**ZrN、CrN 基硬质涂层的制备及其
力学性能、高温氧化行为研究**

**Fabrication, mechanical properties and high temperature
oxidation behaviors of ZrN and CrN based hard coatings**

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**Fabrication, mechanical properties and high temperature
oxidation behaviors of ZrN and CrN based hard coatings**



A Dissertation Submitted to the Graduate School in Fulfillment of
the Requirements for the Degree of

Doctor Philosophy

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摘要

现代加工业的发展,特别是高速切削、干切削工艺的出现以及日益增多的难加工材料,对刀具涂层提出了越来越严格的要求,苛刻的服役条件要求刀具涂层必须具备更高的硬度、耐磨性、高温抗氧化性以及足够的强度和韧性。广泛应用的 TiN、TiC 涂层以及在此基础上发展起来的 TiCN, TiAlN、TiAlCN 等单层/多层硬质涂层,已不能够满足现代加工业的发展对刀具涂层材料提出的更高要求。由于非钛的 ZrN、CrN 基硬质涂层具有优异的力学、高温抗氧化性能以及在加工钛及钛合金、高速干式切削工艺中的优越性,成为目前硬质涂层领域的研究热点。近十年来,研究者们对 ZrN、CrN 基硬质涂层已经开展了相关研究,并且能够制备出一些具有良好的力学性能以及高温抗氧化性能的硬质涂层,但目前仍存在一些难题和挑战,亟待深入研究,譬如涂层的生长以及结构演变过程、涂层的工艺参数-组成、结构-力学性能之间的相互关系以及相关的致硬机理、涂层高温氧化过程中的微观结构演变、Al 元素掺入对提高涂层高温抗氧化性能的作用机制以及寻求新的涂层体系进一步改善硬质涂层的力学及高温抗氧化性能等。

因此,本文以 ZrN、CrN 基硬质涂层为研究对象,系统地研究了反应磁控溅射的工艺参数对 ZrN、CrN 涂层的组成、结构及力学性能的影响,探讨了 ZrN、CrN 涂层的工艺参数-组成、结构-力学性能之间的相互关系以及相关的致硬机理;阐明了 ZrN、CrN 涂层高温氧化过程中的相转变、微观结构演变过程及其对涂层高温抗氧化性能的影响;研究了 Al 元素对 ZrN、CrN 基涂层的力学以及高温氧化抗性能的影响,揭示了 Al 元素对提高 ZrAlN、CrAlN 涂层高温抗氧化性能的本质原因;通过掺入 Y 有效的提高了 ZrN、CrAlN 涂层的力学以及高温抗氧化性能,并深入探讨了 Y 的作用机制,为包括稀土元素在内的反应活性元素在硬质涂层领域的应用提供了理论依据。所取得的主要结论及成果如下:

1、氮气流量百分比对 ZrN 涂层的组成、生长取向以及微观结构的影响主要归结于靶材中毒以及沉积粒子扩散时间的改变;沉积压强以及基体偏压对涂层的生长取向、应力状态以及微观结构的影响主要归结于沉积粒子能量、数量的改变及其对已沉积涂层表面的轰击作用。涂层的致硬机理为取向增强、细晶强化以及应力增强。首次发现了纳米 ZrN 涂层的反 Hall-Petch 效应,并采用修正的 Eshelby

公式估算了纳米结构硬质涂层由 Hall-Petch 效应向反 Hall-Petch 效应转变的临界晶粒尺寸, 理论计算结果与实验观察一致; 提出了一种复合硬度的模型, 解释了反 Hall-Petch 效应的本质原因, 为制备具有优异力学性能的纳米结构硬质涂层提供了理论指导。首次利用高温原位 XRD 以及 TEM 确定了 ZrN 涂层在高温氧化时首先生成 $t\text{-ZrO}_2$, 并逐渐向 $m\text{-ZrO}_2$ 转变的过程, 揭示了 ZrN 涂层高温抗氧化性能较低的本质原因。

2、多种分析方法联用确定了 CrN_x 涂层结构随氮气流量百分比以及靶材功率变化的演变规律。涂层的硬度取决于涂层的化学组成、显微结构以及应力状态。通过控制工艺参数可以实现对 CrN_x 涂层组成、结构以及力学性能的调控。 CrN_x 涂层的高温氧化行为的研究结果阐明了 Cr_2N 涂层的高温抗氧化性能低于 CrN 涂层的本质原因即 Cr_2N 涂层在高温氧化时转变为 CrN, 该转变伴随着 20% 的体积膨胀导致了由相转变生成的 CrN 疏松多孔, 为氧气以及 Cr 离子的扩散提供了快速通道。

3、当 Al 元素含量低于由 fcc 向 hcp 结构转变的临界值时, Al 元素的掺入有效的提高了 ZrN、CrN 涂层的力学以及高温抗氧化性能。 ZrAlN 在高温氧化时生成了非晶 Al_2O_3 包裹 Al_2O_3 稳定的 $t\text{-ZrO}_2$ 的纳米复合结构, 该结构既限制了 $t\text{-ZrO}_2$ 向 $m\text{-ZrO}_2$ 的马氏体相转变, 又降低了氧化层与氮化层的摩尔体积差异, 使得氧化层内孔洞及裂纹等缺陷的数量降低, 从而提高了涂层的高温抗氧化性能; CrAlN 高温氧化时, 由于 Al 元素的选择性氧化, 氧化层为富 Al 的 $(\text{AlCr})_2\text{O}_3$, 结构致密, 有效的降低 O 的内扩散, 使得涂层具有优异的高温抗氧化性能。造成 Al 元素对 ZrAlN 、 CrAlN 涂层高温抗氧化性能提高的作用机制存在差别的本质原因为 $\text{Al}_2\text{O}_3\text{-ZrO}_2$ 、 $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ 的固溶度以及氧势的差异。

4、首次采用 Y 掺入 ZrN 涂层中, 使其在高温氧化时生成 Y_2O_3 稳定的 $t\text{-ZrO}_2$ 氧化层, 降低了由 $t\text{-ZrO}_2$ 向 $m\text{-ZrO}_2$ 的马氏体相变导致的氧化层内裂纹及孔洞的数量, 有效的提高了 ZrN 涂层的高温抗氧化性能; 当 Y 量超过 10% 时, 由于涂层与氧的亲合力以及氧化层内氧空位数量的增加导致涂层的高温抗氧化性能降低。5% 以下的 Y 掺入提高了 ZrN、 CrAlN 涂层的硬度及涂层-基体的结合力。0.6%-1.5% 的 Y 的掺入进一步提高了 CrAlN 涂层的高温抗氧化性能, 使其能够更好地承受高速干式切削过程中的高温服役条件。 CrAlYN 涂层优异的高温抗氧化

性能是基于反应活性元素的“界面中毒模型”。超过 1.5% 的 Y 的掺入在氧化层内生成 YAG 的第二相，急剧降低了 CrAlYN 涂层的高温抗氧化性能。

关键词：反应磁控溅射；ZrN、CrN 基硬质涂层；微观结构；力学性能；高温氧化行为

Abstract

With the development of the modern factory, especially the appearance of high speed dry machining and an increasing number of difficult to machining materials, the requests on hard coatings deposited on cutting tools are more and more restrict. Due to the severe service conditions, the hard coatings must possess higher hardness, better wear and high temperature oxidation resistance, sufficient strength and toughness. The widely used TiN, TiC and further developed TiCN, TiAlN, TiAlCN single layer and multilayer hard coatings will not meet the stricter requests arised from the development of modern factory. Recently, the non-titanium ZrN and CrN based hard coatings have drawn much attentation from the researchers engaged in hard coatings as a result of their higher mechanical properties, better high temperature oxidation resistance and superior performance in machining titanium metals and alloys, and high speed dry machining. In the latest ten years, several researches on ZrN and CrN based hard coatings have been carried out and some hard coatings with excellent mechanical properties and high temperature oxidation resistance have been fabricated. However, there are still many difficulties and great challenges to be further investigated, including the growth and microstructural evolution of hard coatings, the relationship among working parameters-composition, microstructure-mechanical properties and the relevant hardening mechanism, microstructural evolution of hard coatings during high temperature oxidation process, the action mechanism of Al alloying inducing the promoted high temperature oxidation resistance of hard coatings and the search for new systems to further improve the mechanical properties and high temperature oxidation resistance of the hard coatings.

The ZrN and CrN based hard coatings were selected as the objects of this thesis. The influence of working parameters of reactive magnetron sputtering on chemical composition, microstructure and mechanical properties of ZrN and CrN based hard coatings were systematically investigated, to explore the relationship among working parameters-composition, microstructure-mechanical properties and the relevant

hardening mechanism. The phase transition, microstructural evolution and their influence on the high temperature oxidation resistance of ZrN and CrN based hard coatings were clarified. The influence of Al alloying on the mechanical properties and high temperature oxidation resistance of ZrN and CrN based hard coatings. The intrinsic reasons accounting for the promoted high temperature oxidation resistance of ZrAlN and CrAlN coatings were then revealed. The mechanical properties and high temperature oxidation resistance of ZrN and CrAlN coatings can be further improved by Y ttrium addition. The relevant action mechanisms of Y addition were deeply researched, which would provide the theoretical basis for the application of the reactive elements including the rare-earth elements in hard coatings. The major conclusions and achievements are outlined as follows:

1. The influence of nitrogen flow percentage on the chemical composition, growth orientation and microstructure of the ZrN coatings was dependent on target poision and the variation of diffusion times of the adatoms, while the influences of working pressure and substrate bias on the growth orientation, stress and microstructure were relying on the energy and quantity of adatoms and their bombardment effect on as-deposited coatings. The hardening mechanisms included texture strengthening, refined grain strengthening and stress hardening. We found the inverse Hall-Petch effect in the nanocrystalline ZrN coatings for the first time and we estimated the critical grain size of the transition between Hall-Petch effect and inverse Hall-Petch effect using the modified Eshelby equation. The theoretical results were in good agreement with those of experimental observation. We proposed a composite hardness model to explain the inverse Hall-Petch effect. These findings would provide a new strategy to fabircate superior mechanical properties of nanostructured hard coatings. We used high temperature in-situ X-ray diffraction and transmission electron microscopy to confirm the microstructural evolution of ZrN during high temperature oxidation, and it revealed that during oxidation t-ZrO₂ initially formed and it gradually transited to m-ZrO₂. The intrinsic factor inducing the worse high temperature oxidation resistance of the ZrN coatings was clarified for the first time.

2. The nitrogen flow percentage and working pressure inducing microstructural

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